ROTATING UNIT FOR PREPARATIVE-SCALE GAS CHROMATOGRAPHY

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INTRODUCTION

Preparative-scale gas chromatography offers the attractive possibility of separating simultaneously and in a pure state several components, even if they form a non-ideal mixture. This is not possible by other physical methods of separation.

A number of preparative-scale units have been described which employ a column having a larger diameter than the analytical one or a fixed set of columns operating in parallel[1,2]. Some of these systems have been automatized by means of a time programme or by detector output[3,4]. SCOTT[5] obtained a continuous separation by a countercurrent movement of the stationary phase against the carrier gas flow and a similar arrangement is described by BARKER AND CRITCHER[6].

We describe below a unit* by which a continuous separation is achieved with a set of columns which is moved transversely to the carrier gas flow.

THEORY

We assume that the column is moving parallel to itself with a speed V_s with respect to the feed and collecting systems (which for simplicity are supposed fixed). Then the column assumes consecutively the positions shown in Fig. 1 (dotted lines), while the carrier gas is flowing in the direction of the arrows through the column.

Calling l the chromatographic column length and t_{ri} the retention time of a generic component i, the path of this latter, in the plane of the figure, makes an angle with the vertical line given by:

$$\tan \alpha_i = \frac{V_s\, t_{ri}}{l}$$

The elution of the component will be in the position defined by the relation:

$$x_i = V_s\, t_{ri} \qquad (1)$$

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* Patent application No.: *Ital. Pat.* 4274/60; *Ger. Pat.* 1A-21-422; *French Pat.* 855–858; *Japan. Pat.* 8123/61; *Brit. Pat.* 8453/61; *Swiss Pat.* 2760/61; *U.S. Pat.* 95706.

In fact, owing to longitudinal diffusion, the elution of the component will occur in a range Δx_i proportional to the band broadening, Δt_{ri}.

When a sequence of columns is moved into the appropriate positions at successive instants, the process is made continuous: the component distribution in the trap-system is the space equivalent of the elution diagram that a single column gives in time (*i.e.*, Fig. 4).

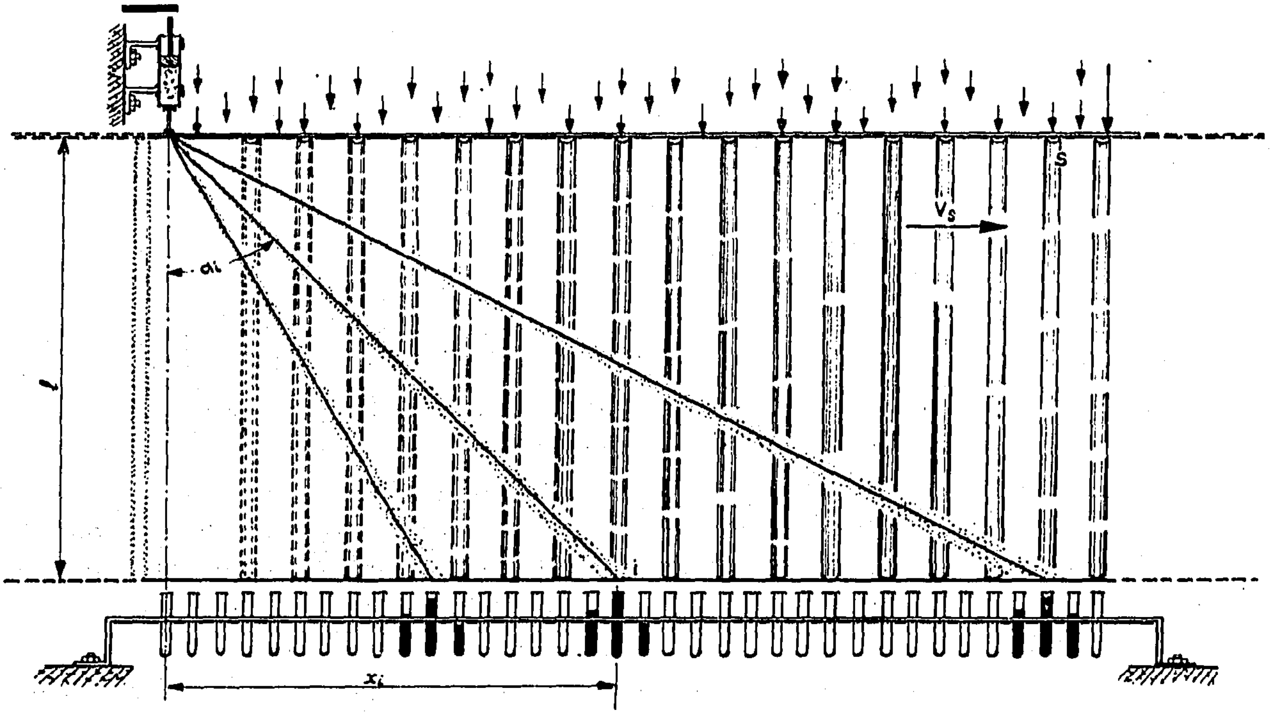


Fig. 1.

It follows that the system does not require a detector for its operation and performs the separation and the analysis at the same time. Further, the process is made completely automatic by arranging the columns on a cylindrical surface. Calling r the cylinder radius and w the angular velocity, eqn. (1) becomes

$$x_i = wrt_{ri} = 2\pi rnt_{ri} \tag{2}$$

where n is the number of revolutions of the cylinder in unit time.

The condition for maximum efficiency is obtained when the last component (retention time t_{rM}) is eluted adjacent to the first component (retention time t_{rm}). This means that the t_{rM} component follows on the ideal cylindrical surface a path which is longer than the one corresponding to a complete revolution.

In this case the set speed is

$$V_s \simeq \frac{2\pi r}{t_{rM} - t_{rm}}$$

and the frequency of revolution is

$$n \simeq \frac{1}{t_{rM} - t_{rm}} \tag{3}$$

The frequency of revolution may also be influenced by other conditions, *i.e.* maximum feed rate, maximum purity, position of traps in which a component has to be collected, and so on.

The previous treatment would also be true for a continuous bidimensional stationary phase in movement but in this case the band broadening due to transverse diffusion makes the separation impractical[7].

APPARATUS

The unit is shown in Figs. 2 and 3. It consists of a set of 100 columns (6 mm i.d., 1.2 m in length) rotated by means of a constant speed motor ranging from 1 to 50 r.p.h.

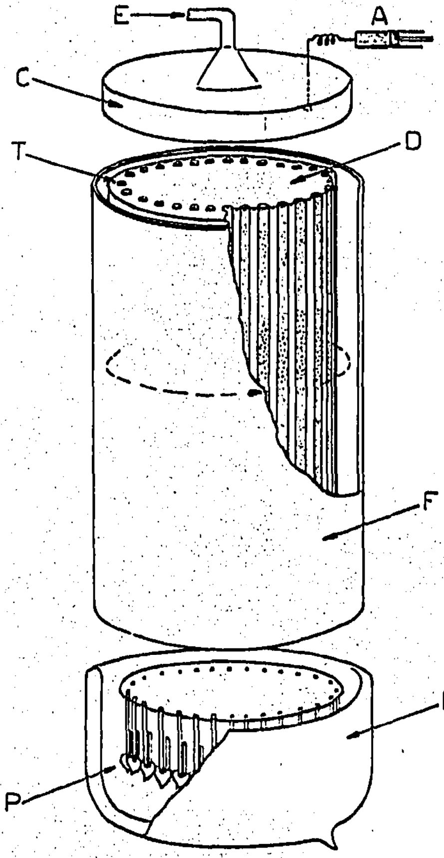


Fig. 2. Preparative-scale gas–liquid chromatography unit. (A) Sample feed; (C) Gas-tight cover; (D) Top cover-plate; (E) Carrier gas inlet; (F) Heating jacket; (P) Collecting traps; (R) Cooling bath.

The carrier gas (nitrogen or air) flows through the gas-tight head into all the columns except the one column to which the feed is being added at that instant.

The feeding is accomplished through a fixed block, with a hole drilled through it, sliding on a flat ring to which are welded the tops of the columns. The sliding block and the flat ring are the only parts which need precision machining.

If the sample is liquid, it is vaporized by a preheater. In the lower part of the apparatus, the cylindrical set of columns slides over a further ring to which the trap-system is connected; the receiver assembly is immersed in a bath of coolant.

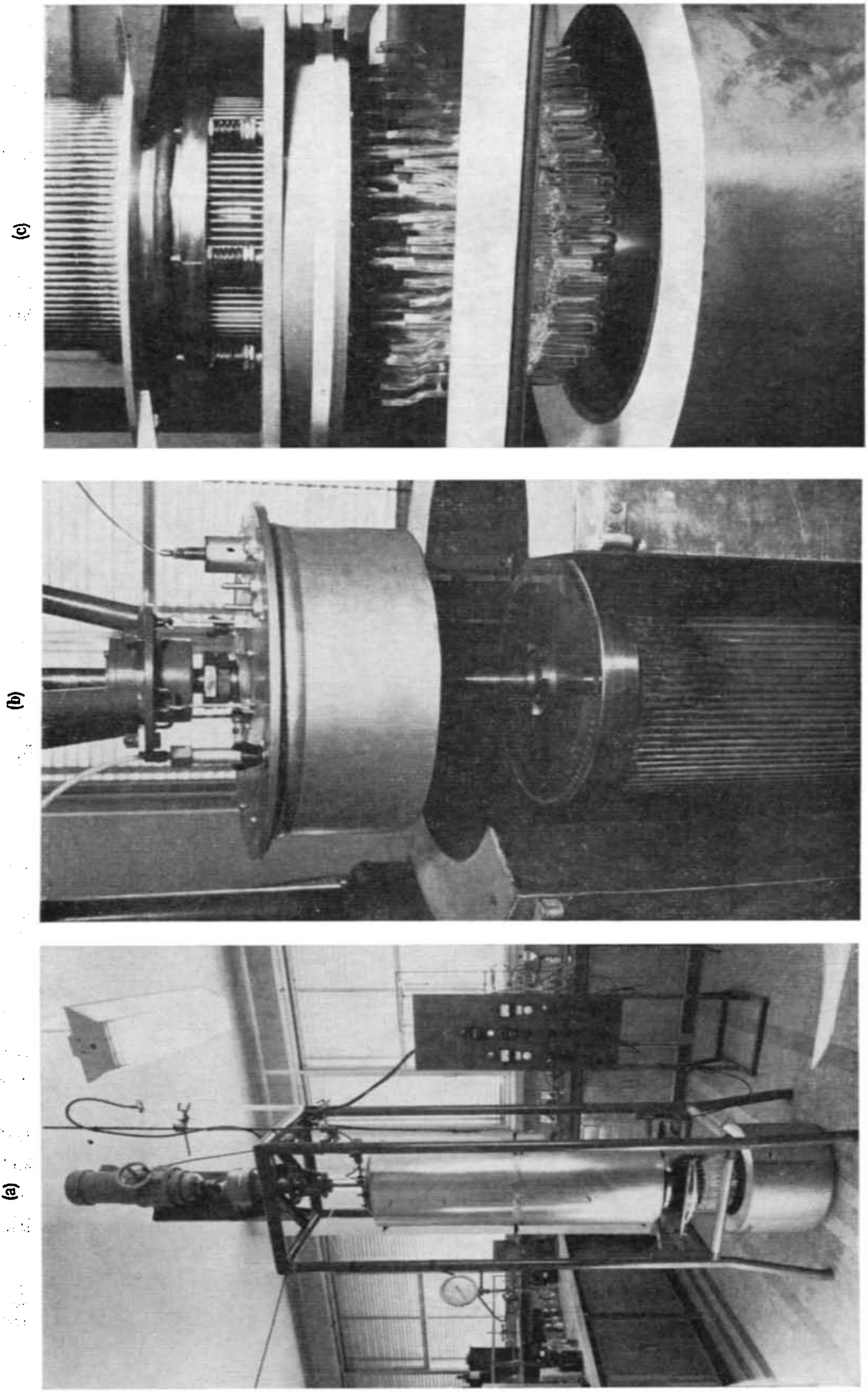


Fig. 3. Preparative-scale gas-liquid chromatography unit. (a) General view of unit; (b) Gas-tight cover and heads of columns; (c) Collecting system.

An electrically-heated jacket maintains the set of columns at the desired operating temperature. A single pilot column, identical to the unit columns but provided with a detector and related recorder and control device, is used for calculating the running conditions and for estimating in advance the elution ranges of components.

APPLICATIONS

In spite of the limitations imposed on the unit owing to overall dimensions (columns of limited length, large number of receivers in place of a few manifolds for collecting the eluted bands, etc.), the preparative-scale chromatographic apparatus has operated successfully both from the theoretical standpoint and from the point of view of its usefulness.

It is possible to establish in advance from equation (1) the number and position of the receivers in which the components will collect. This is demonstrated by the separations reported below:

Example 1. Mixture: *n*-Heptane–toluene (1:1, v/v)

Feed rate: 60 ml/h
Number of r.p.h.: 10
Temperature: 92°
Carrier gas pressure: 1 atm
Stationary phase: polyethylene glycol 400

Relevant receiver positions (*initial–maximum–final*):

Calculated	*n*-heptane 9–11–24;	toluene 70–85–3
Found	*n*-heptane 8–10–22;	toluene 72–86–4.

Example 2. Mixture: *n*-hexane–acetone (1:1, v/v)

Feed rate: 20 ml/h
Number of r.p.h.: 21
Temperature: 94°
Carrier gas pressure: 1.3 atm
Stationary phase: tricresyl phosphate

Relevant receiver positions (*initial–maximum–final*):

Calculated	*n*-hexane 20–24–27;	acetone 35–44–52
Found	*n*-hexane 20–24–29;	acetone 35–44–55

A most interesting point concerns the relation between the maximum possible feed rate and the desired purity of the components separated. It is well known[8] that the relation between base width of peaks (time measured Δt) and the sample size q (when this is sufficiently large) is approximately linear:

$$\Delta t = Kq + c \tag{4}$$

where K and c are constants at the fixed temperature and pressure. From the definition of resolution[9] for two components having retention times t_{r1} and t_{r2}

$$S_{12} = 2 \frac{t_{r2} - t_{r1}}{\Delta t_1 + \Delta t_2} ,$$

the condition which allows the calculation of maximum feed rate for the column is given by $S_{12} = 1$ with the condition of a purity higher than 99.9 % throughout the bands of the two components. This then gives the result

$$q_M = 2 \frac{t_{r2} - t_{r1}}{a} - \frac{b}{a} \tag{5}$$

where a and b are constants, directly related to those in eqn. (4). It follows that the maximum feed rate admissible for the whole set of columns is given by

$$Q_M = N q_M n \tag{6}$$

where N is the number of columns and n the number of revolutions per unit time.

Thus the maximum feed rate calculated from eqn. (6) for a separation with a purity of more than 99.9 % of a mixture benzene–cyclohexane at 80°, on tricresyl phosphate, results in a value of 220 ml/h. In practice, the expected purity was obtained at a rate of 200 ml/h.

Similarly, in the separation of *n*-heptane–toluene the maximum feed rate calculated for a purity 99.9 % was 180 ml/h, in good agreement with the results shown in Table I. From these data it is also possible to see how the purity decreases as the feed rate increases. A load of 1 l/h allows purities of practical interest.

TABLE I

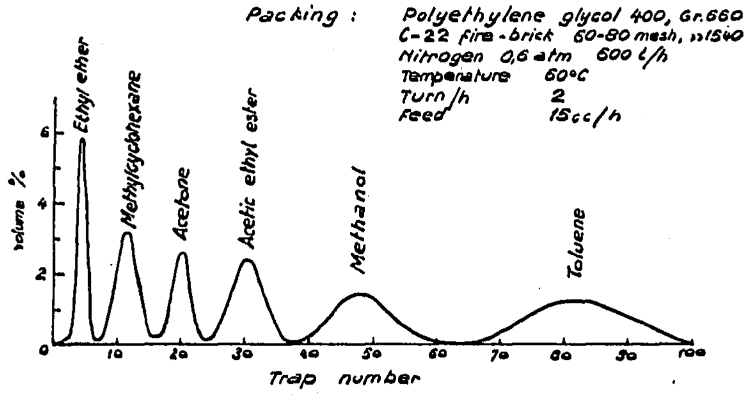
VARIATION OF PURITY WITH FEED RATE

Mixture: *n*-heptane–toluene (1:1, v/v). Stationary phase: polyethylene glycol 400 (660 g) supported by C22 fire-brick, 60–80 mesh (1540 g). Carrier: nitrogen, 1050 l/h. Temperature: 95°. r.p.h.: 6.

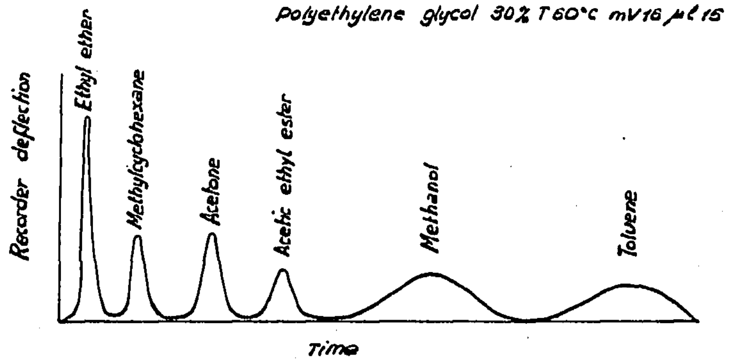
Feed rate ml/h	*Fraction n-heptane*						*Fraction toluene*					
	Head cut		*Central cut*		*Tail cut*		*Head cut*		*Central cut*		*Tail cut*	
	Purity	*% vol. of fraction*	*Purity*	*% vol. of fraction*	*Purity*	*% vol. of fraction*	*Purity*	*% vol. of fraction*	*Purity*	*% vol. of fraction*	*Purity*	*% vol. of fraction*
200	99.99	6.2	99.99	92.9	99.70	0.9	99.80	0.6	99.96	97.9	99.93	1.5
300	99.80	0.6	99.91	98.0	99.70	1.4	99.70	1.6	99.95	97.1	99.92	1.3
400	99.84	1.9	99.90	96.7	99.84	1.4	99.55	1.6	99.96	97.1	99.79	1.3
500	98.30	0.5	99.90	98.2	99.65	1.3	99.78	1.3	99.98	97.1	99.96	1.6
1000	87.00	3.7	98.50	94.9	50.10	1.4	49.90	1.6	99.60	94.7	86.00	3.7

Another very important feature of our apparatus is that the eluted component is cut off at the end of the column without any passage through detector or valve and so on, which can cause trouble owing to dead space. In such a way the overall efficiency of the unit is the same as that of a single analytical column: Fig. 4 shows the equivalence between the time picture (elution diagram) and space volume distribution, obtained with a six-component mixture.

The apparatus described appears to be a satisfactory solution for a preparative-scale working unit. Furthermore, the energy consumption is comparable with that of a high efficiency distillation, and the ratio of feed rate to the amount of stationary liquid required is high.



DISTRIBUTION IN SAMPLE COLLECTION SYSTEM.



CHROMATOGRAM

Fig. 4.

ACKNOWLEDGEMENTS

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SUMMARY

An efficient preparative-scale gas–liquid chromatography unit is described, in which a continuous separation is carried out by moving a drum of columns transversely to the carrier gas flow.

Performance studies indicate that the overall efficiency of the apparatus is the same as that of a single column, and the ratio of feed rate to the amount of stationary phase is sufficiently high to be of practical interest.

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